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A High-Temperature Furnace and a Heating/Drawing Device Designed for Time-Resolved X-Ray Diffraction Measurements of Polymer Solids Using Imaging Plates

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For time-resolved X-ray diffraction measurements using the imaging plate system in the drawing and/or heating process of polymer solids, a high-temperature furnace for heat treatment and a heating/drawing device were newly designed and constructed. Then, to demonstrate their performance, some experimental results obtained in the drawing process of an extruded/blown film of high-density polyethylene at room temperature and in the crystallization process of an oriented amorphous film of poly(ethylene naphthalene-2,6-dicarboxylate) by heating were presented. Other experimental results obtained using them were also briefly cited.

KEY WORDS: High-Temperature Furnace/ Drawing Device/ Stretching/ Oriented Crystallization/ X-ray Diffraction/ Imaging Plate

1. INTRODUCTION

In the melt-processing of a crystallizable synthetic polymer into a factory product such as a uniaxially or biaxially stretched film, fibers, *etc.*, it is quite important to leave inherent excellent properties of the polymer for such a product and to give some additional characteristics to the product in compliance with its use. In particular, the degree of chain orientation and the crystallinity influence significantly the performance of the final product. Uniaxial drawing is frequently used as one of the ways to orient the molecular chains and to promote crystallization. There are several procedures to obtain higher orientation of polymer chains by uniaxial drawing such as: 1) crystallization by heating from an oriented amorphous solid which was made by drawing, 2) crystallization by cooling from a melt oriented by drawing, 3) drawing/crystallization of a polymer solid at a high temperature, 4) drawing of a polymer solid which was crystallized beforehand. So far, there have been many investigations of structural formation by drawing[1] and of structural change accompanied by phase transition in the drawing process[2]. As known well, high-strength/modulus fibers have been developed by ultra-drawing of polyethylene [PE] of ultra-high molecular weight[3] and by zone-drawing of verious polymers[4].

We have studied the structural changes of various polymers due to uniaxial drawing by

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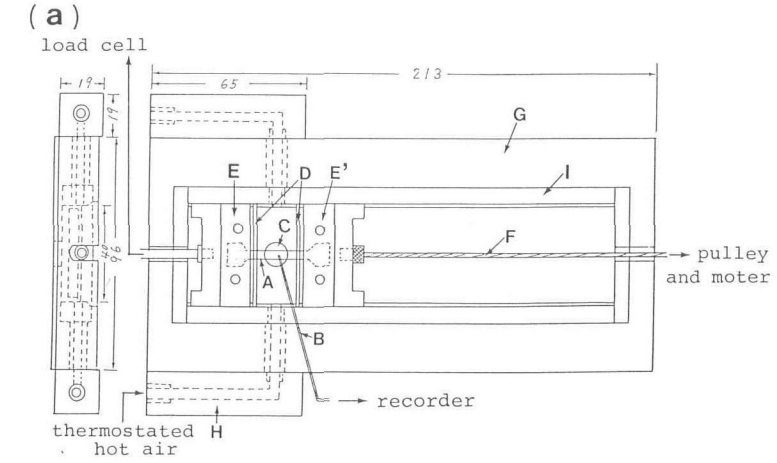
using X-ray diffraction. Present-day rotating-anode X-ray generators have been greatly advanced, for example owing to improvement in the vacuum technology, to be of high power: the generator used in this study is a 60kV-300mA type (Rigaku-Denki, RU-300). In addition, X-ray detectors of high performance have also been developed, such as a TV system equipped with an image orthicon camera[5,11], which system can record one 2-dimensional diffraction pattern within one second, and an imaging plate [IP] system[6]. The IP is 5～6 times more sensitive against X-ray than highly sensitive X-ray photoemulsions, and has a wide dynamic range: each pixel (0.125 mm ×0.125 mm) of IP can store the integrated X-ray intensity of a dynamic range up to 10^5. Before the advent of such highly sensitive detectors, X-ray diffraction photograghs were taken before and after deformation (or processing) and the structural difference between them was discussed. Using the highly sensitive detectors mentioned above, however, the structural changes of specimens during deformation/processing can be followed as a time-resolved series of X-ray diffraction/scattering patterns. The desired X-ray sources and detectors, therefore, are now available, but no apparatuses suitable for drawing/heating of polymer films/fibers are on the market because the apparatuses must be designed for individual purposes depending upon the kinds of specimen and the experimental conditions. Thus we have tried to construct a heating/drawing device and a high-temperature furnace, both of which are appropriate to investigate structural changes of polymer solids using the X-ray diffraction system equipped with IP. In this report, the mechanism and performance of the device and furnace will be mentioned, and then some experimental results obtained using them will be demonstrated.

2. CONSTRUCTION OF THE HEATING/DRAWING DEVICE AND THE HIGH-TEMPERATURE FURNACE

2.1. Heating/drawing device

Formerly a heating/drawing device for the X-ray TV system had been constructed and used for the study on the structural change accompanied by phase transition in the drawing process of PE: the specimen was stretched vertically in this device (prototype)[5]. The device is, therefore, modified for X-ray measurement using IP. As shown in Fig. 1, the new heating/drawing device is designed and constructed so that the specimen is to be stretched in the horizontal direction. In this device, the specimen temperature is controlled by blowing thermostated hot air vertically into the specimen chamber in order to attain a uniform distribution of temperature over the whole specimen and to raise the specimen temperature as quickly as possible up to a given temperature. To prevent heating up of the chucks (E and E' in Fig. 1(a)) which are to clamp the ends of specimen, two partition strips (D) are introduced between the chucks; of course, the strips are to be located outside the specimen area that is stretched and illuminated with the X-ray beams. The specimen temperature, namely the temperature of the air in the specimen chamber, is monitored with a chromel-alumel [C-A] thermocouple (B) placed in the vicinity of the specimen area which is illuminated with the X-ray beams. Outside the metal inner framework (I in Fig. 1(a)) of the device, *bakelite* (G) is used for thermal insulation against the open air. The precision of temperature regulation is within ±1°C at a specimen temperature between room temperature [RT] and 160°C: Figure 2 is an example which demonstrates well the precision of temperature regulation. The load cell (J



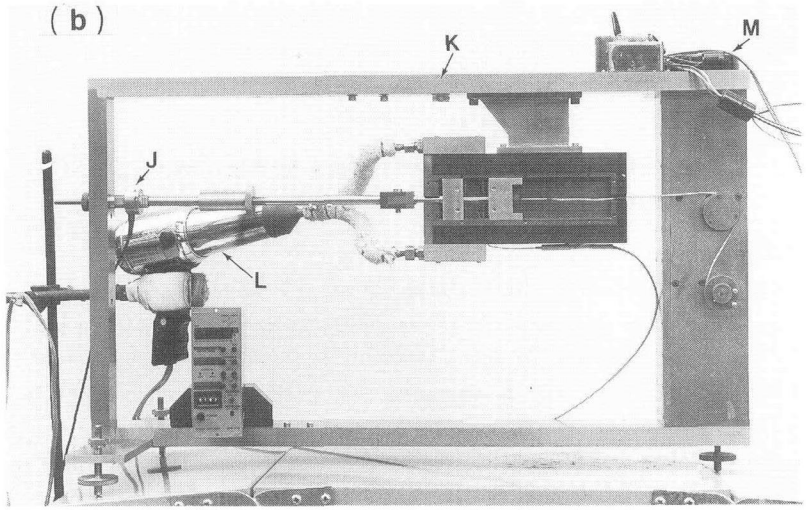


Fig. 1. Heating/drawing device.
(a)Sketch of the heating/drawing chamber.
A: specimen, B: C-A thermocouple, C: beryllium window, D: partition strips, E,E': chuck, F: wire to pull the chuck (E'), G: thermal insulator (*bakelite*), H: thermal insulator (*micalex*), I: metal inner framework.
(b)Whole view of the device.
J: load cell, K: metal outermost framework, L: hot air blower, M: moter to drive the check (E') in (a).

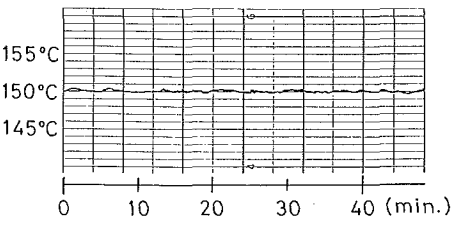


Fig. 2. Example of the output of the C-A thermocouple (B in Fig. 1(a)), demonstrating well the precision of temperature regulation in the specimen chamber of the heating/drawing device.

in Fig. 1(b)) can be attached to the chuck (E), which is fixed to the outermost framework (K in Fig. 1(b)), in order to measure the magnitude of stress during stretching.

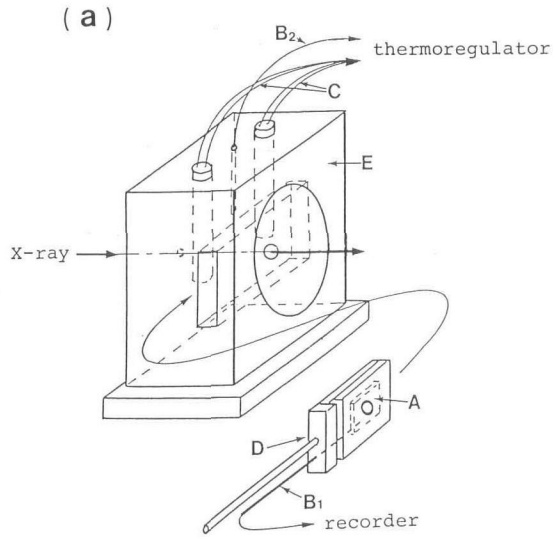
2.2. High-temperature furnace

The high-temperature furnace for X-ray measurement using IP has been newly constructed (see Fig. 3). The chamber (E) is made up of copper. Two rod-like heaters (C) are introduced into the copper block as shown in Fig. 3(a). The temperature of the chamber is to be monitored/controlled using a C-A thermocouple (B_2). The outside of the chamber is thermally insulated from the open air using *micalex*: this is a heat-stable material developed by TOSHIBA. The working temperature range of this furnace is from RT to 500°C. The specimen temperature is monitored with a C-A thermocouple (B_1) which has been inserted into the specimen holder (D). The precision of temperature regulation is within ± 0.5°C for a given temperature between RT and 200°C and within ± 1°C for 200°C through 500°C. The specimen holder is made up of copper: a specimen (A) is set between two small plates of copper. The holder in which a specimen has been set is introduced into the furnace at RT for gradual heating with an increase in temperature or into the pre-heated furnace for heat treatment at a given constant temperature. A mica window is attached to (E) at the exit for scattered X-ray. For heat treatment, say at 180°C, it needs only 30 sec to reach 97% of the expected equilibrium temperature after introducing the holder into the furnace which is thermostated beforehand at 180°C. After such gradual heating or isothermal heat-treatment, the specimen holder is taken out of the furnace, and then might be, for example, immediately transfered into ice-cold water for quenching.

3. EXAMPLES OF X-RAY DIFFRACTION MEASUREMENTS USING THE HEATING/DRAWING DEVICE AND THE HIGH-TEMPERATURE FURNACE

3.1. Stretching of extruded/blown [E/B] films of high-density PE using the heating/drawing device[7]

In melt-processing a crystalline polymer, the crystallites are sometimes oriented with a certain crystallographic plane of them being parallel to a surface of the final product of the polymer. For example, in the E/B film of high-density PE, the (001) planes are preferentially oriented parallel to the film surface. Figure 4(a) is the wide-angle X-ray diffraction [WAXD] pattern when the X-ray beams are incident onto such a film in the direction perpendicular to



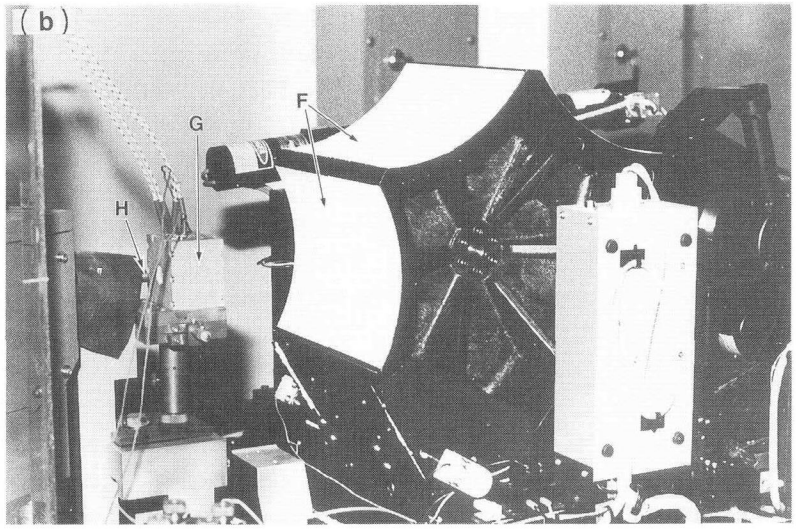


Fig. 3. (a)Sketch of the high-temperature furnace.
A: specimen, B_1,B_2: C-A thermocouple, C: heaters, D: specimen holder, E: copper block.
(b)Whole view of the X-ray diffraction system equipped with IP.
The high-temperature furnace is set in the system.
F: IP, G: high-temperature furnace, H: pinhole collimator of 0.5 mm diameter.

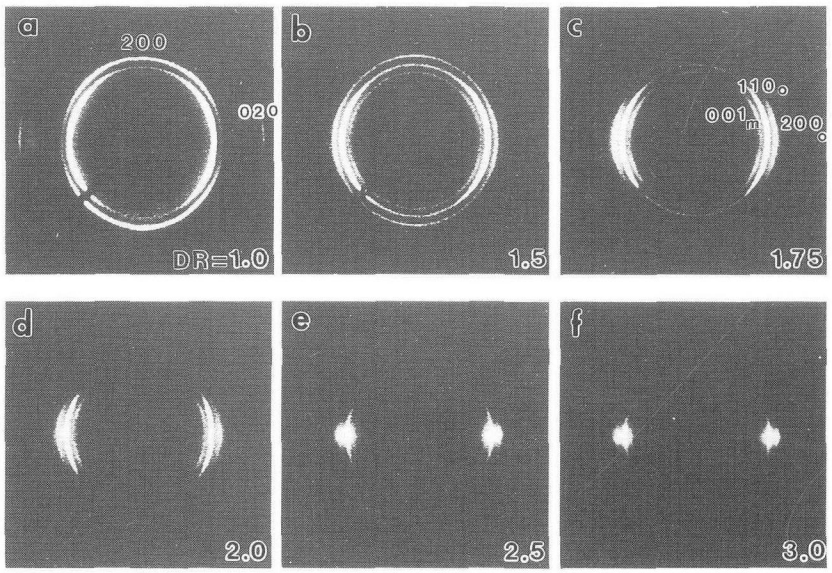


Fig. 4. Change in the WAXD pattern from an E/B film of high-density PE during drawing at room temperature [RT] and a drawing rate of 5 mm/min along MD. The X-ray exposure time is 10 sec for each pattern. The specimen thickness is 0.3 mm (15 films). The figure written and the oblique dark rod in each pattern show a draw ratio [DR] and the beam stop, respectively. The drawing direction is vertical.

its surface: in this figure, *machine direction* [MD] is vertical. In the meridional direction, namely in the vertical direction of Fig. 4(a), the strong arc-shaped (200) reflection is observed. The (110) reflections which are stronger than the (200) one are also observed inside of the (200). The maxima of these arc-shaped (110) reflections are located in the off-meridional directions, *viz.* in the diagonal directions of Fig. 4(a). The weak (020) reflection is observed on the equator. Consequently, the crystallographic **a**-axis is preferentially oriented parallel to MD, and naturally is parallel to the film surface. The **b**-axis is also parallel to the film surface but perpendicular to MD, *viz.*, parallel to *transverse direction* [TD]. As known well, the **b**-axis is the growing direction of crystalline lamellae. The **c**-axis is, thus, perpendicular to the film surface. The left half of Fig. 5 illustrates the arrangement of crystallites in such an E/B film of high-density PE.

Figure 4 shows a time-resolved series of WAXD patterns of the E/B film, which were obtained using the new heating/drawing device during stretching at room temperature [RT] along MD, namely in the **a**-axis direction. Just before the onset of necking, the monoclinic reflection appears inside the (110) one of the orthorhombic form: according to Seto and others[8], this monoclinic reflection comes from the crystallographic (001) plane parallel to the chain axis (**b**-axis), which plane corresponds to the orthorhombic (110) plane. When necking takes place, the orthorhombic (200) and (110) reflections and the monoclinic (001) one start to move together onto the equator. At a draw ratio [DR] of about 2, some of the crystalline lamellae are broken and the film partly shows a fiber structure in which the **c**-axis (chain axis) of the

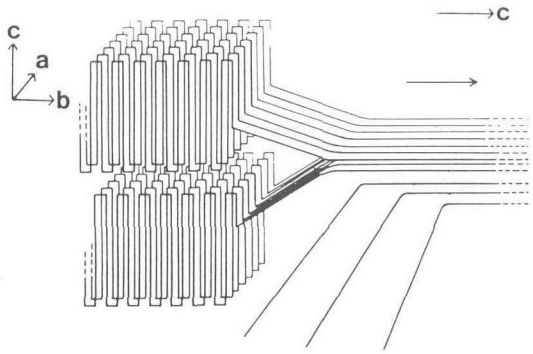


Fig. 5. Schematic illustration of the arrangement of crystallites in an E/B film of high-density PE, and that of the transformation of the lamellar structure to a fiber structure *via* unfolding.[10]

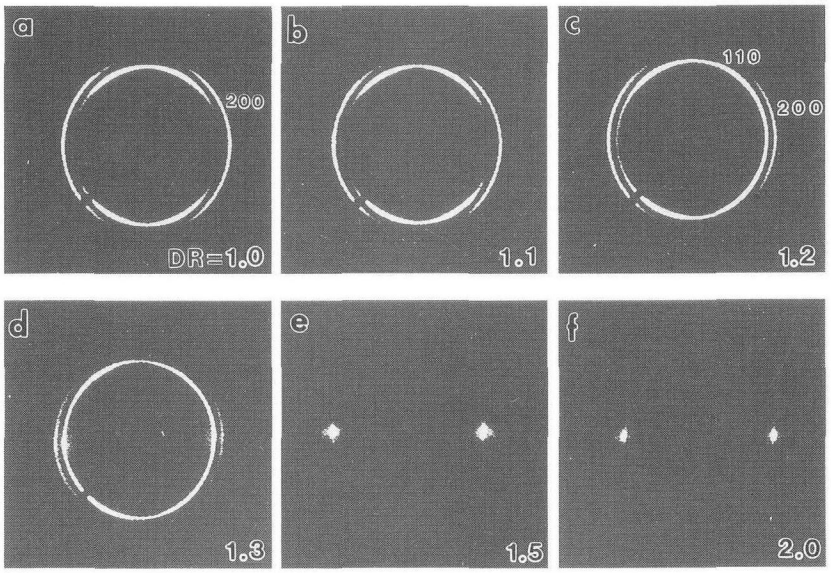


Fig. 6. Change in the WAXD pattern from an E/B film of high-density PE during drawing at room temperature [RT] and a drawing rate of 5 mm/min along TD. The X-ray exposure time is 10 sec for each pattern. The specimen thickness is 0.3 mm (15 films). The figure written and the oblique dark rod in each pattern show DR and the beam stop, respectively. The drawing direction is vertical.

orthorhombic form is aligned in the stretching direction. By the way, as to the estimation of DR during stretching with the device except for DR =1 and the final DR, for example, Ref. 9 should be consulted.

Figure 6 shows a time-resolved series of WAXD patterns of the E/B film, which were obtained using the heating/drawing device during stretching at RT along TD, namely in the **b**-axis direction. At DR =1.3, necking takes place and the corresponding WAXD pattern (Fig. 6(d)) shows the onset of the **c**-axis orientation (fiber orientation). In this case, however, no monoclinic reflections are observed. From Figs. 4 and 6, we deduce as follows: In stretching the E/B film along MD, the crystalline lamellae are bent, twisted and then broken, and finally the film comes to have a fiber structure with re-arranging polymer chains and being accompanied by phase transition. On the other hand, in stretching the E/B film along TD, there occur no bending nor twisting of lamellae, and the transformation of the lamellar structure to a fiber structure appears to occur *via* successive unfolding proposed by Kobayashi[10] (see Fig. 5) due to stress concentration in the film.

Structural changes of the E/B film during stretching isothermally along MD at various temperatures were also investigated using the heating/drawing device in question: The monoclinic reflection appeared definitely in the drawing process below 50°C. Though the faint monoclinic reflection was observed in drawing at 60°C, it was not recognized above 70°C. Detailed discussion on these results will be reported elsewhere[7].

Using this heating/drawing device, the following experiments for various kinds of specimens have been done:

1) We investigated the structural change in the drawing process of ultra-high-molecular-weight [UHMW] PE.[6,11]

2) Highly drawn films of UHMW PE reactor powder were stretched further at a constant rate of drawing and a high temperature, showing that deformation proceeds after transition of the hexagonal form to orthorhombic one.[12]

3) There have been recognized two crystalline forms (α and β) in poly(tetramethylene terephthalate). Transition from α to β by adding a tensile stress was traced using the device.[13]

4) Stress-induced transition from the 4_1 helix to 24_7 one of polyvinylcyclohexane was examined using the device.[14]

5) Comparison of ultra-drawing behaviour between the gel-like spherulite press method and the gel-casting method was carried out using two kinds of specimens prepared from solution of UHMW PE, between which only the cooling rate of solution was greatly different.[15]

6) When an unoriented amorphous film of poly(ethylene naphthalene-2,6-dicarboxylate) [PEN] was drawn at 150°C, the film exhibited a fiber structure accompanied by a lattice distortion due to the axial shift of neighbouring chain stems relative to one another along the chain axis. The film, thereafter, frequently showed the uniplanar axial orientation in which naphthalene rings in the chain are preferentially aligned parallel to the film surface.[9]

3.2. Crystallization of an oriented amorphous PEN film by heating using the high-temperature furnace[9]

When an unoriented amorphous film of PEN is stretched below its T_g (=117°C), it can be elongated up to a DR of 4~5 *via* necking and becomes an oriented amorphous film. Figure 7

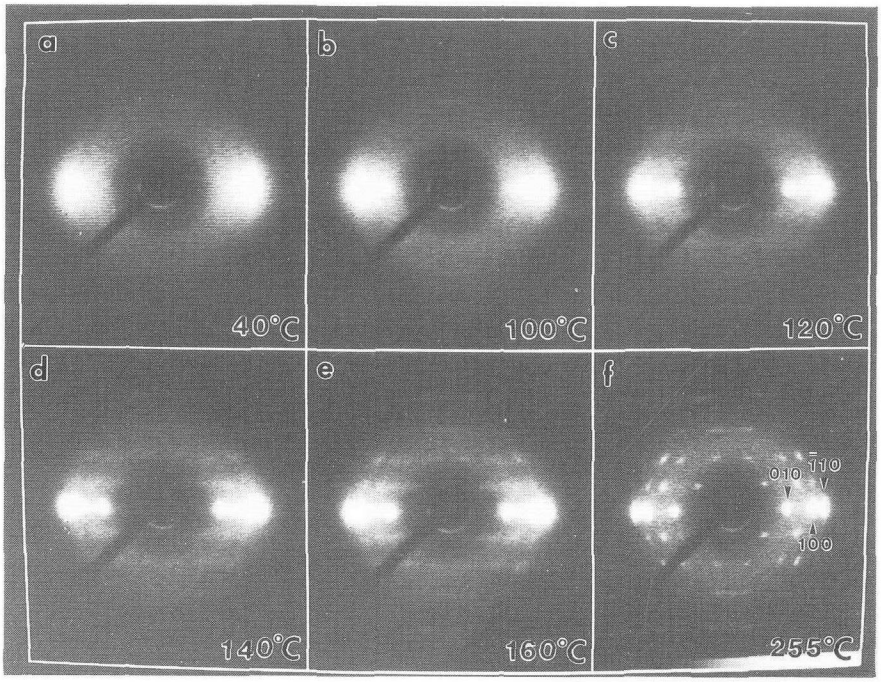


Fig. 7. Change in the WAXD pattern from the oriented amorphous film of PEN in the heating process at a heating rate of 3°C/min: the film had been made beforehand by drawing an unoriented amorphous film at 65°C to DR = 3.6.[9] The figure written and the oblique dark rod in each pattern indicate a specimen temperature and the beam stop, respectively. The drawing direction is vertical.

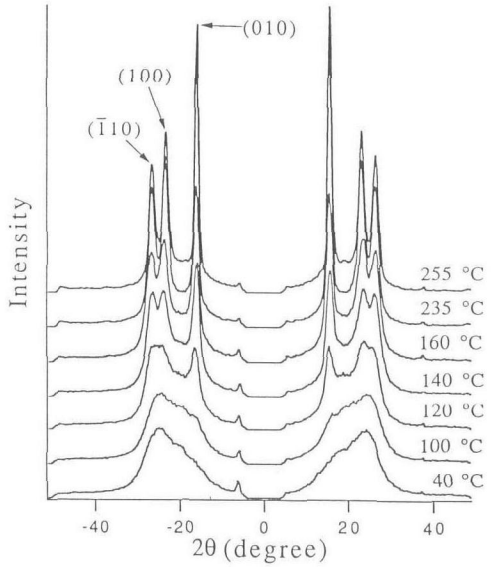


Fig. 8. Intensity profiles on the equator of the WAXD patterns of Fig. 7.[9] 2θ is the scattering angle (θ: Bragg angle). The figure written on the right-hand side of each profile indicates a specimen temperature.

is a time-resolved series of WAXD patterns from the pre-oriented amorphous film of PEN in the heating process at a heating rate of 3°C/min using the new high-temperature furnace: the pre-oriented film was made by drawing an unoriented amorphous film to DR = 3.6 at 65°C. Figure 8 shows the change in the equatorial intensity profiles of the WAXD patterns of Fig. 7. In the unoriented amorphous film, crystallization started at about 185°C. Figures 7 and 8, however, well demonstrate that crystallization begins just above T_g, for example even at 120°C, in the oriented amorphous film. As illustrated in Fig. 7, the crystalline reflections on the equator become sharper with increasing temperature above 120°C, being accompanied by streaks on the off-equatorial layer lines: the streaks come from the lattice distortion mentioned before. In addition, the profile obtained at 255°C in Fig. 8 shows that the (010) reflection is much stronger than the others and its width at half-maximum is smaller than those of the others: the profile, thus, indicates a fiber orientation with fairly high crystallinity though it also suggests the presence of slight uniplanar axial texture. It should be noted here that the value of specimen temperature written in Figs. 7 and 8 corresponds to that at the mid-time of each X-ray exposure (2 min) to the IP in the heating process.[9]

Using this high-temperature furnace, we investigated the phase transition of triphenylene hexa-n-octanoate in the heating process.[16]

4. CONCLUDING REMARKS

In order to investigate the structural formation during drawing, crystal growth, structural changes accompanied by phase transition and so on, we have designed and constructed the heating/drawing device and the high-temperature furnace for X-ray measurement. The prototypes of the device and furnace were utilized, being combined with the X-ray TV system. The new device and furnace have been utilized for X-ray measurement, being combined with the IP system. For example, using the new heating/drawing device, we could catch well the monoclinic reflection in the drawing process of high-density PE[7] and UHMW PE[6,11] as described in 3.1: because this reflection disappears immediately when drawing is discontinued, it is not easy to catch it by WAXD photographing. The device, however, should be modified further so as to move both the chucks clamping the ends of a specimen at an identical speed in order to suppress shifting away of the specimen area during stretching, which area is illuminated by X-ray beams. In addition, the maximum working temperature of the device should be raised up to, at lowest, 250°C. We are planning on designing and constructing such a more improved heating/drawing device for time-resolved X-ray measurements using the IP system.

REFERENCES

(1) For example, N. Kasai and M. Kakudo, *J. Polym. Sci.: Part A*, **2**, 1955 (1964); T. Asano and T. Seto, *Polym. J*, **5**, 72 (1973).
(2) T. He and R. S. Porter, *Polymer*, **28**, 1321 (1987); T. Kanamoto and O. Ohtsu, *Polym. J*, **20**, 179 (1988).
(3) P. Smith and P. S. Lemstra, *Makromol. Chem.*, **180**, 2983 (1979).
(4) T. Kunugi, S. Oomori and S. Mikami, *Polymer*, **29**, 814 (1988).
(5) K. Shimamura, S. Murakami and K. Katayama, *Bull. Inst. Chem. Res., Kyoto Univ.*, **55**, 269 (1977).
(6) A. Kawaguchi, S. Murakami, K. Katayama, M. Mihoichi and T. Ohta, *ibid.*, **69**, 145 (1991).
(7) S. Murakami *et al.*, in preparation.

(8) K. Tanaka, T. Seto and T. Hara, *J. Phys. Soc. Japan*, **17**, 873 (1962).
(9) S. Murakami, Y. Nishikawa, M. Tsuji, A. Kawaguchi, S. Kohjiya and M. Cakmak, *Polymer*, **36**, 291 (1995).
(10) K. Kobayashi cited by P. H. Geil in "Polymer Single Crystals", Interscience, New York, p.473 (1963); M. Horio, *Intern. Polym. Processing*, **1**, 1 (1986).
(11) A. Kawaguchi, S. Murakami, M. Tsuji, K. Katayama and T. Ohta, *Sen-i Gakkaishi*, **48**, 427 (1992).
(12) H. Uehara, T. Kanamoto, A. Kawaguchi and S. Murakami, *Polym. Prepr., Japan*, **42**, 1479 (1993).
(13) A. Kawaguchi, Y. Nishikawa and S. Murakami, *Polym. Prepr., Japan*, **43**, 1531 (1994).
(14) Y. Nishikawa, A. Kawaguchi and S. Murakami, *ibid*., **43**, 1532 (1994); Y. Nishikawa, A. Kawaguchi, S. Murakami and S. Kohjiya, *Proc. ISF '94, Yokohama*, p.39 (1994).
(15) T. Ohta, T. Wachi, M. Mihoichi, A. Kawaguchi, S. Murakami and K. Katayama, *Polym. Prepr., Japan*, **40**, 837 (1991); T. Ohta, A. Takada, T. Yamamura, A. Kawaguchi and S. Murakami, *Polymer*, in press.
(16) S. Kobayashi, K. Sayama, T. Hoshino, Z. Osawa, A. Kawaguchi and S. Murakami, *Prepr. 18th Liq. Cryst. Symp., Niigata Univ*., p.388 (1992).